CHAPTER 13

Spectrochemical Analysis

To AN EVER-INCREASING EXTENT, the spectrograph is being used to determine the composition of a wide variety of materials and to fix the concentration of their constituents. Known to the chemist as qualitative and quantitative analysis, respectively, these spectroscopic techniques are commonly referred to as spectrochemistry or spectrochemical analysis, often without the adjectives qualitative and quantitative, and, for the most part, these terms are used to mean analysis by emission spectroscopy.

The development of spectrochemical analysis is, of course, an outgrowth of the recognition, about the middle of the last century, that the spectrum emitted by an atom is characteristic of that atom and of its energy condition. It has already been pointed out in Chap. 1 that Kirchhoff and Bunsen were the first to recognize this principle clearly and to use it in the isolation and discovery of two new alkali elements, caesium and rubidium. It is now known, of course, that the absorption and emission spectra of molecules, also, are characteristic of their components and structure.

13.1. Qualitative Spectrochemical Analysis

The work by Kirchhoff and Bunsen constituted the first qualitative analysis. These experimenters noted, after a study of the spectra of the known alkali elements, that certain spectral lines not belonging to the pure spectra of the known alkalies appeared in the light emitted by some of their preparations. Search for the origin of these lines led finally to the isolation of the new elements. During this same period, Kirchhoff studied the Fraunhofer lines and identified numerous elements in the sun's atmosphere. Qualitative spectrochemistry was firmly established by these achievements. It has, of course, been extended in scope, precision, and sensitivity by later work.

Today, under proper conditions, the spectrograph provides the most rapid and, at the same time, the most sensitive technique for qualitative analysis. In Sec. 9.9, the procedures have been discussed for determining from the spectrum what elements are present in a source or for deciding whether or not any atom or molecule is present in detectable amounts. The attributes of various light sources which are suitable for spectrochemical investigations have been discussed in Chap. 2. Further details of the applications of these techniques will be pointed out here.

For qualitative analysis by emission spectroscopy, the light source and spectrograph selected will be those that are adapted to the nature and available quantity of the sample. For solid, conducting samples, a d-c or a high-voltage a-c arc is sensitive, controllable, and generally convenient; the sample may be of almost any size or shape and may be mounted in any suitable electrode holder. The spark, also, may be used between solid electrodes, but the resultant sensitivity to trace concentrations is much less. For materials with low melting or ignition points, water- or air-cooled electrode holders may be desirable; in any case, the current strength must be held at levels that will not lead to overheating the electrodes. In fact, except when required for a steady arc, high current values are almost never necessary or desirable. For most purposes, a current of from three to five amperes is satisfactory. The more volatile constituents in the sample will ordinarily appear in the arc spectrum first; materials of high boiling point will appear later and, in some cases, will not appear at all until the more volatile materials have been, to a large extent, exhausted. It is desirable, therefore, to adjust the intensity of the source image on the slit in such a way that an exposure of at least one or two minutes is possible.

Poorly conducting or refractory materials, or materials available in minute amounts only, may be packed in cavities drilled in a graphite, silver, or copper lower electrode. Unless it is essential to eliminate the cyanogen bands (3500A to 4200A) that are emitted strongly by graphite arcs in air, graphite is to be preferred. It has fewer emission lines and the arc attains higher temperatures; the sensitivities in analysis are therefore higher. The so-called spectrographic carbons, supplied by several companies, do not contain the traces of the alkali and earth-alkali metals or of other impurities found in ordinary pure arc carbons; they have been removed, usually by heating the carbon in vacuo to white heat. Rods of $\frac{5}{16}$ inch or $\frac{1}{4}$ inch diameter are satisfactory; the cavity can be made with a clean drill of slightly smaller size. The carbons should be handled with clean tweezers, and the samples should be cleaned and handled carefully, because contaminations are easily picked up from the hands or tools. If the material is nonconducting, or if it does not pack well, it may be mixed with powdered graphite. For solutions, a concentrated drop or two can be dried on the tips of graphite electrodes. As alternatives, the solution may be atomized into a flame, as has been done by Lundegårdh,[1] or excited in a spark discharge to a liquid surface, as, for example, by the method of Duffendack, Wiley, and Owens.[2] For qualitative purposes, however, these procedures seem not so convenient or so rapid. In all these cases, the upper electrode is usually of the same material as the lower; if it is pointed, the arc will wander less and burn more uniformly. When foreign material, such as graphite, is used, control exposures must be run with the blank electrodes to determine the impurities, if any, as well as the lines emitted by the electrodes themselves. It must be borne in mind, however, that when the sample material is later placed in or on the electrodes, the changed electrical gradients and temperatures in the arc may bring out lines that were seen only faintly, if at all, in the control tests.

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[1] H. Lundegårdh, *Zeits. f. Physik*, 66, 109, 1930.

[2] O. S. Duffendack, F. H. Wiley, and J. S. Owens, *Ind. Eng. Chem.*, 7, 410, 1935.

The nature of the sample is the important consideration in the choice of a spectrograph, because the dispersion must be enough to separate the spectral lines of the various likely elements, and the region covered must include their sensitive lines. Inspection of the tables of ultimate or persistent lines will show that the most persistent lines for only ten elements lie in the region between 4600A and 9000A, and that for all of these there are also persistent lines between 4600A and 2000A. Moreover, for many elements, there are no persistent lines between 4600A and 9000A, although, of course, all have some spectral lines there. In view of these facts, glass spectrographs are not well suited to qualitative analysis because of their limited range, especially if the detection of small amounts of material is involved. Quartz spectrographs and gratings covering the region from 4600A to 2000A are, however, satisfactory. Even medium- and small-sized quartz spectrographs have produced good results, although larger instruments are better because their greater dispersion makes line identification more certain and reduces the difficulty from interfering lines of other elements. For the heavy metals or the rare earths, a grating or a large quartz spectrograph is almost essential. A spectrograph of large aperture is needed only for samples that are extremely small and, therefore, can provide only short exposures; standard spectrographs, with their higher dispersion and longer exposures, are preferable in all other cases. Similarly, emulsions of good contrast are preferable to high-speed emulsions; their sensitivity to faint lines is less, but so, too, is their response to background spectrum, and when fast emulsions are used, the increase in background is likely to mask any improvement in the intensity of faint lines.

Identification of elements spectroscopically requires care and judgment, and some knowledge, based on experience or on study of the theory of spectra, of the behavior of the elements in different light sources and in different matrices. The best indication of the presence of an element is the detection of its ultimate or persistent lines. The relative intensity, however, depends to some extent on the source and spectrograph: in strong spark discharges, the sensitive arc lines, as compared with the sensitive spark lines, may be greatly suppressed; the characteristics of the photographic emulsion, the intensity distribution of the grating, or the transmission of the prism may produce relative line intensities notably

different from those given in a particular chart or table. Each spectroscopist, on the basis of experience with his equipment, should build up his own list of sensitive lines, their relative intensities, and their behavior.

The identification of an element can rest on only one line if there is no possibility of confusion with lines of other elements at approximately the same wave length, or if the constituents are limited to a few possibilities. Usually, however, a minimum of two must be observed, especially if the sample spectrum is rich in lines, and they should be ultimate or persistent lines and should have the correct relative intensities. If the ultimate lines belong to a multiplet or line group arising from the same electron configuration, all lines of the group must be accounted for. Possible interfering lines of other elements in the sample, known or suspected, must always be considered.

The number of elements that can be detected spectrochemically is given by some as 55, by others as 70, and by still others as 75. What is meant by these statements is that the number of elements indicated have sensitive lines that can be excited in solid samples, by arcs or sparks in air, and photographed on ordinary emulsions. The elements omitted from these counts are hydrogen, the noble gases, the halogens, carbon, nitrogen, oxygen, and sulphur, and from the smaller lists, also the rare earths and the metalloids. These omissions are justified on the basis of the limitations stated above, and there is the further limitation that spectroscopically-pure test samples of these elements and spectrum charts including them are not easily available. Hilger's R. U. powder, for example, contains 50 elements, and the charts of Gatterer and Junkes, which are the best available, cover 73. All elements, however, have lines in the ordinary photographic region that can be excited under appropriate conditions. The gases, for example, can be excited in various kinds of discharge tubes. Gatterer and Frodl[3] have demonstrated the detection of the halogens in compounds, by placing small, solid samples in the positive column of a discharge tube, and McNally, Harrison, and Rowe[4] have excited them in a hollow-cathode discharge. The same procedure was followed for the metalloids, with equal success. The spectra of the rare earths are now well enough known to make spectroscopic methods preferred over the difficult chemical separations. With improvement in light sources and techniques, qualitative analysis of every element will be feasible and, in cases of complex or refractory samples or of chemically difficult analyses, preferable to chemical methods.

The various elements in the sample may be in combined or uncombined form. The temperature of the ordinary sources is sufficient to dissociate any molecules and excite the resulting atoms. In fact, it is a weakness of emission spectroscopy that it gives little information as to the molecular arrangement of the atoms in the source material, but, at the same time, it is often an advantage that the total amount of an element can be measured, regardless of the various compound forms in which it may be present.

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[3] A. Gatterer and V. Frodl, *Ric. Spectroscop.*, 1, 201, 1946.

[4] J. R. McNally, Jr., G. R. Harrison, and E. Rowe, *J. Opt. Soc. Am.*, 37, 93, 1947.

13.2. Trace Detection

In qualitative spectrochemistry, the major constituents of the source material are readily recognized from the sensitive and other prominent lines of these elements. An extremely important question in many analysis problems, however, is the identification of trace elements, which may be of importance even when present in amounts not detectable by conventional chemical methods. Many examples of the sensitivity of spectrochemical analysis for the determination of various elements in different sources and in the presence of other major constituents are to be found in the literature cited and in other papers in the field.

There are, in fact, wide variations in the relative spectral sensitivity of the different elements and of the various light sources: arcs are, in general, much more sensitive than spark sources, and the spectra of the metals much easier to excite then those of the metalloids. The properties of an element in relation to those of other elements in the sample must also be taken into account: an element of low boiling point, high vapor pressure, or low ionization potential will be excited more strongly than elements in the same sample with higher boiling points or ionization potentials, or with relatively lower vapor pressures at the electrode temperatures.

Under favorable conditions, however, the presence of an element in concentrations as low as one part in a million is detectable. Owens,[5] who used solutions dried on the tips of graphite electrodes, reported, in the analysis of caustic liquors, an absolute sensitivity of as little as 1×10^{-6} mg of the test element on the electrodes, and a relative sensitivity for manganese as low as 0.000002 per cent. On the other hand, there may be cited the unfavorable example of van Tongeren's[6] determination of tin in minerals. Using a glass spectrograph, with the cathode layer of a d-c arc as the source and with the powdered sample mixed with graphite and sodium carbonate and packed in the cavity of a graphite electrode, he reported 0.3 per cent of tin in SnO_2 as the least detectable concentration. His results, however, would certainly have been greatly improved if the much more sensitive ultraviolet tin lines could have been used rather than those in the visible (glass spectrograph) region.

There are very few elements for which a relative sensitivity of 100 parts per million cannot be attained; a sensitivity of 10 to 20 parts is common; and 0.1 part is reached in some cases. The absolute sensitivity varies between about one-tenth and one one-thousandth of a microgram, even though the total sample may not be larger than 10 or 20 micrograms. These sensitivity limits, in most cases, were determined by testing progressively weaker concentrations until the ultimate lines were no longer detectable against the plate background. Kaiser[7] has suggested that it would be more meaningful to define the least detectable amount as the amount such that the density difference of the ultimate line from the background is $3 \cdot \sqrt{2}$ times the mean fluctuation of the blackening, a difference that he considers to be just certainly measurable. Then, from measurements on two or more samples of small, known concentrations, the analytical curves discussed in Sec. 13.4 can be drawn, the uncertainty of blackening measurement determined, and the concentration corresponding to Kaiser's criterion read from the curve. In a test for the sensitivity of determination of zinc in pure aluminum, with an interrupted arc, a controlled spark with 0.8 millihenries of inductance, and a controlled spark with no added inductance, Kaiser found sensitivities of 0.0004 per cent, 0.007 per cent, and 0.02 per cent, respectively. Since the sensitivity of trace determination depends on the spectrograph, the photographic plate, the light source, and the spectral region used, as well as on the other elements present in the sample, it is best, if previous experience in comparable cases is lacking, to undertake some comparative tests on samples of known, similar composition before reaching a conclusion as to whether or not an element is present in appreciable amount. It must be borne in mind that the absence of the detection lines of an element indicates merely that the element is not present in sufficient amount to be detected with the source and equipment used.

When the utmost sensitivity in trace detection is desired, attention must be given to all details of the procedure. The example given by Kaiser shows a factor of sensitivity of 50 between three good light sources; similar differences may exist between different plates and spectrographs. In fact, two perfectly proper spectrographic arrangements may differ by a factor of 10,000, or more, in their sensitivity of detection on the same sample. A major case of difficulty is background in the spectrum; the high background in the inductance-free spark spectrum cited by Kaiser undoubtedly accounts for the fact that the sensitivity was much lower than in the case of the interrupted arc. Attention to the proper choice of source is only one of the means by which background can be reduced. Others are: changing to a spectrograph of higher dispersion, so that the background energy is spread over a longer distance; using the optimum slit width, since background intensity is proportional to slit width; using a plate of higher contrast to keep background near or below the plate inertia; and eliminating, as far as possible, the background caused by scattered light or emulsion processing.

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[5] J. S. Owens, *Ind. Eng. Chem.*, 11, 59, 1939.

[6] W. van Tongeren, *Chemical Composition of the Earth's Crust in the East Indian Archipelago.* Amsterdam: Centen, 1938.

[7] H. Kaiser, *Spectrochim. Acta*, 3, 40, 1947; also contains a bibliography of published data on sensitivities for various sources and kinds of materials.

In general, under suitable working conditions, the sensitivity of trace analysis by line emission methods is better than that of chemical wet methods and as good as, or better than, that of colorimetric methods. The speed is usually greater, especially if suitable master charts or spectra are available for rapid identification or comparison. The specimens can ordinarily be used in their natural form: as solid electrodes; as solutions dried on the ends of graphite, silver, or copper electrodes; as powders or nonconductors packed in cavities in graphite electrodes. A few minutes is sufficient to expose and process a plate, and the spectra can be examined rapidly in all but the most complicated cases.

The detection of traces of impurities in samples is, of course, an important function of spectrochemical analysis. No less important is the rapid identification of the elements present and the determination of the ones, if any, that need to be analyzed quantitatively by the more time-consuming chemical methods. Many examples of this sort of analysis will be found in the *Proceedings of the Summer Conferences on Spectroscopy and its Applications*, listed in the bibliography at the end of this chapter. In this connection may be mentioned the classification of minerals; the detection of metallic poisons in criminal investigations; and the sorting of scrap steels as to alloy type in steel mills, which may, in fact, be done with a visual spectroscope (page 90).

It can be seen from the foregoing discussion that the applications of qualitative analysis with the spectrograph are as varied as those of chemical methods. The spectrographic method has the great advantages of speed and simplicity in a technique that can handle a wide variety of samples with the same equipment and procedure.

13.3. Quantitative Spectrochemical Analysis

The earliest practical applications of the spectrograph were qualitative, and these are still the best known, but they can hardly be successfully carried out without some understanding of the quantitative use of the spectrograph. To an increasing extent, the two techniques are used in conjunction. Moreover, quantitative spectrochemistry has gained rapidly in use and acceptance and probably has become the more important.

Quantitative spectrochemical analysis is based on the fact that when a series of specimens made up of two or more elements contains one element in small and decreasing amounts, its spectral lines grow gradually weaker and disappear in a definite order and their intensities are simple functions of the concentration, whereas the relative and absolute intensities of the spectral lines of the major constituents remain unchanged. An example of the influence of concentration on the strength of spectral lines is seen in Fig. 106, which shows a series of iron spectra containing small, known percentages of manganese. As nearly as possible, the spectra were made under identical conditions, as is shown by the uniform intensity of the marked iron lines. It will be noted that the manganese lines decrease in intensity with decreasing concentration and disappear at different percentage contents in the sequence.

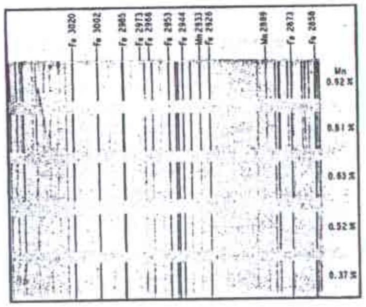

Fig. 106. Spectrograms of samples of iron containing manganese in different amounts.

The first clear statement of the relationship between concentration and the character of the spectral lines was made by Lockyer.[8] In 1872 and 1873, in three papers before the Royal Society of London, he discussed the possibility of quantitative analysis with the spectroscope, and in another paper, with W. C. Roberts, Chemist of the Mint, he described some observations on alloys of copper and gold, and of zinc and cadmium. Lockyer stated, "A change in the percentage of any constituent of a metallic alloy ordinarily causes a change in the character of the lines exhibited in the resulting spectrum, in length, brightness or thickness; and the percentage of the constituents might be determined by comparison with the spectra of percentages of known composition." The first systematic study of quantitative analysis was made in 1882, by Hartley,[9] at Dublin, and he appears to have made the first successful quantitative analyses: those of beryllium in cerium compounds, and magnesium and calcium in limestone.

Hartley, and his immediate successors, such as Pollock, at Dublin, and de Gramont, at Paris, made their analyses by comparing visually the spectra of their samples with those of a graded series of samples of similar and known composition, and by choosing the known spectrum which best matched that of the unknown sample. Such methods of matching spectra, especially if there is not careful selection and control of the source, can be expected to give only the roughest accuracy, perhaps 10-25 per cent at best, because the intensity of the spectral lines of a minor or secondary component in a source is influenced, not only by the characteristics of the spectrographic apparatus and by the photographic technique, but also by the nature and amount of other elements in the electrodes and by random fluctuations in the operation of the source. The development of quantitative spectrochemical analysis in recent years, which has followed from careful study of each step of the process, has resulted in more consistent and controllable light sources, better photographic materials, more direct comparison methods, and, above all, precise photometry of spectral-line intensities. It now attains an accuracy comparable to that of chemical analysis, and a speed much greater.

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[8] J. N. Lockyer, *Phil. Trans.*, **163**, 253 & 639, 1873, and **164**, 479, 1874; J. N Lockyer and W. C. Roberts, *Phil. Trans.*, **164**, 495, 1874.

[9] W. N. Hartley, *Phil. Trans.*, **175**, 325, 1884.

13.4. The Internal-Standard Principle

In spite of all these improvements in technique, precise and rapid spectrochemical analysis would be difficult, if not impossible, if it were still based on the use of external reference standards, i.e., on the comparison of the relative intensities of spectral lines from the analysis sample with those from reference standard samples taken separately and, possibly, at a different time and on a different plate. There are unavoidable small fluctuations in emulsion sensitivity, in emulsion processing, and, even in the best of sources, in excitation conditions, and they would be major and uncontrollable causes of error. Present-day precision analysis was made possible by the development, by Gerlach,[10] in 1926, of the internal-standard method, and at present, almost without exception, all precision quantitative analysis utilizing emission spectra is based on some variant of this principle. As noted earlier, a major difficulty in all methods of matching spectra arises from light-source fluctuations, which can result in spectra of unequal over-all intensity and intensity distribution from samples of identical composition. Gerlach observed that many of these difficulties of "external reference standards" are avoided when a chosen line of the element under analysis is compared with a line of some reference element in the same spectrum. Qualitatively, at least, the two lines will respond in the same way to random source fluctuations —they cannot do so exactly unless both lines have identical excitation functions and unless both elements have identical vapor tension-temperature relations.

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[10] W. Gerlach, *Foundations and Methods of Chemical Analysis by the Emission Spectrum*, Chap. V. London: Adam Hilger, Ltd., 1929.

For each of several known concentrations of the element under analysis, Gerlach's method is to choose a reference pair consisting of a line of the analysis element and a line of the reference element of equal intensity at that concentration. It is assumed that if the two lines of a reference pair appear with equal intensity in the spectrum of any sample, the concentration of the analysis element will be the same as in the reference sample whose spectrum had been previously studied. Analysis of an unknown sample can then be carried out by selecting visually the one of these reference pairs in the spectrum for which the two lines are of equal intensity. Most of the modern procedures use only one such pair of lines. Their relative intensities are determined by some photometric procedure and plotted as a function of concentration. The resulting graph serves as the basis for the determination of the concentration of any unknown sample. If the two variables are plotted on logarithmic scales, the resulting *analytical curve*, or *working curve*, over a considerable range is usually very close to a straight line. An example from the determination of manganese in iron is given in Fig. 107.

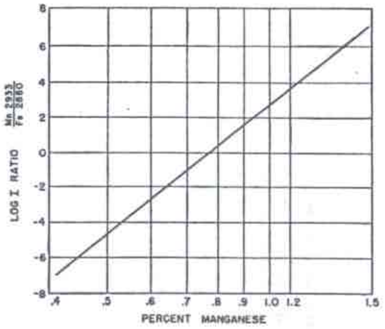

Fig. 107. Analytical curve. The relationship is shown between percentage content of manganese in the sample and the relative intensities of the analysis line-pair.

In practically all cases, it is impossible to select a reference element that has spectral lines whose response to source fluctuations is exactly the same as that of neighboring lines in the spectrum of the unknown element. It is therefore essential to select a pair of lines that behave as similarly as possible under varying conditions; such line-pairs were called by Gerlach *homologous pairs*. Since proximity in wave length avoids variation in plate contrast, and proximity on the plate minimizes errors due to variation in emulsion sensitivity from point to point, a rough selection of line-pairs may be made by choosing a reference element of approximately the same ionization potential and vapor pressure as the analysis element, and then choosing from the two elements a pair of lines which, for the median concentration to be determined, have about equal intensities, are near together, and, if possible, arise from transitions between atomic levels of about the same energy values. In any case, the density of the reference line should fall within the working range of density of the analysis line—in general, in the density range from 0.3 to 1.0.

In the case of liquid or powdered samples, the internal-standard material can readily be added. From the wide range of choices, an element of proper excitation properties can often be found. Furthermore, the amount of reference material added will determine, within a considerable range, the relative intensities of the desired reference line and the analysis line. In the case of solid samples, it is desirable to find a reference line from the spectra of those matrix constituents that are present in amounts sufficiently large to insure that their line intensities will be unaffected by any likely variation in the minor constituents.

Many suitable line-pairs will be found mentioned in the literature of spectrochemical analysis. The choice is influenced by the source conditions used, as well as by the percentage range of content to be covered. Ordinarily, not all the conditions outlined above can be fulfilled. Every effort should be made, however, to choose the best available pair, because the final accuracy of the analysis is largely dependent on a proper choice. It is always advisable, in undertaking a new analysis problem, to test several possible alternative line-pairs. Measurements should be made on the spectra of four or more samples of known composition covering the analysis range. If the intensity ratios are plotted against concentration on logarithmic scales, as in Fig. 107, variations will ordinarily be found for the different pairs, both in the slope of the resulting analytical line, and in the extent of scatter of the individual points about the line. A pair should be selected which gives a good slope, to insure good sensitivity in the determination, and as little scatter as possible, to insure good repeatability or accuracy. The accuracy, however, should be checked by several tests on the same sample. If possible, variations in the operating conditions of the light source should be made to check the constancy of the relative intensity of the pairs and, therefore, their effectiveness in minimizing errors caused by source fluctuations.

13.5. Choice of Light Sources

The accuracy attainable is greatly influenced by the choice of light source, as are also the sensitivity and the analytical range. In fact, under the best modern procedures, the controlling error is that introduced

by the random fluctuations of the light source.[11] The ideal spectrochemical light source would be one in which each element in the electrode would be vaporized into the discharge, regardless of what other elements were present, at a fixed and unvarying rate, and in which the atoms of each element, once vaporized, would be excited to radiate a spectrum in which the spectral lines varied in intensity with concentration, according to an invariable and definite law.[12]

In all ordinary light sources, however, the relative intensities of the lines of any one element and of lines of different elements vary from instant to instant, for a variety of reasons. In electrical discharges, fluctuations in temperature, caused by current variation or ventilation changes, result in fluctuations in the relative intensities of lines with different excitation functions. The potential gradient in a discharge is affected by the ionization potential of all the atoms present and so depends on their kind and number. Further, the rate and order in which different elements evaporate from the electrodes into the discharge depends on the relative vapor pressures and boiling points of the other elements present, as well as on local variations in electrode temperature. While the effects of the worst fluctuations are eliminated by the internal-standard method, there are still wide variations in the errors introduced by light sources. Accordingly, it is important to select the light source carefully and to make certain of its best adjustment. Flames, arcs, sparks, and gaseous discharges all have their fields of usefulness.

The flame has been strongly advocated by Lundegårdh. (See page 21.) His method, spraying a solution into an acetylene-air flame, is especially suitable for biological analyses, such as those of soil, plant, and animal samples, and for the analysis of readily soluble inorganic material. Lundegårdh applied it to 34 of the commoner metallic elements and found the sensitivity to be from 0.001 to 0.000001 mol per liter. Since high concentrations can be handled by simple dilution of the sample, the method is applicable to almost any initial concentration. Suitable reference elements are readily introduced into the solutions. The error is reported as never in excess of 5 per cent of the amount present, and often not more than 1 or 2 per cent. This accuracy is as good as that secured with the best of other sources, but the method has not been widely adopted in this country, no doubt because of the somewhat greater convenience of arcs and sparks for most types of samples.

As has been noted earlier (Sec. 2.3), the d-c arc, in spite of its simplicity and its high sensitivity in the detection of traces of impurities, is subject to erratic fluctuations that limit it, in quantitative work, to problems requiring only moderate precision. To a large extent, the difficulties are due (page 22) to the wandering of the cathode spot, with resultant variations, not only in the temperature of the discharge, but also in the location of the disengaging spot on the cathode and in the duration of disengagement from any one spot. Elements of low boiling point enter the discharge more rapidly and are depleted from the disengaging area more rapidly than elements of higher boiling points.[13] Fluctuations follow in both the relative and the total number of the different kinds of atoms entering the discharge. The arc, then, varies both in intrinsic brilliance and in total intensity and volume, as well as in the relative distribution of intensity among the different spectral lines.

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[11] H. H. Grossman, R. A. Sawyer, and H. B. Vincent, *J. Opt. Soc. Am.*, **33**, 185, 1943.

[12] For a recent discussion of spectrochemical light sources, see *A. S. T. M. Tech. Publ.*, No. 76, 1948.

With these variations in the temperature, volume, and density of the discharge, there is, of course, a related variation in the extent of the absorption, by the outer layers, of the radiation from deeper within the discharge. By Kirchhoff's Law (page 8), the atoms of the outer layers absorb those wave lengths which they are themselves able to radiate. The result is a varying self-absorption, especially of the lines involving the lower energy states of the atom, which produces a greater or less "self-reversal" of the lines. Except for the most strongly reversed lines, which may appear as two lines or wings with a more or less completely absorbed center, the effect of partial self-reversal is a variation in the apparent intensity of the lines affected. For light sources which do not operate at very low pressure, where absorption is small, varying self-reversal is a serious cause of fluctuation in the relative intensities of different lines in the spectrum.[14]

To some extent these variations will average out over the whole exposure. This averaging process can be furthered by including the results of two or more exposures. Actually, no amount of averaging can remove the difficulty entirely, since the relative and absolute intensity variations are not linear in the variables and often not even systematic. It is usually difficult to reduce the source errors below 10 per cent.

These difficulties are particularly marked with d-c arcs between metallic electrodes, especially those, such as iron, that are subject to oxidation in the arc. However, with graphite electrodes and proper electrode shape and current size, reasonable control is possible. In using the graphite electrodes, the precautions described in Sec. 13.1 must be observed. The sample is often burned to complete consumption to avoid difficulties from differential evaporation of the various elements in the arc. Used in this way, the d-c arc is a valuable source for irregular, poorly-conducting, or small samples. For highly refractory materials, such as ores, ceramics, and abrasives, it is, in many cases, the most practical.

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[13] D. Richardson, *Proc. Fifth Summer Conf. on Spectroscopy*, 1937, page 64. New York: John Wiley and Sons, Inc., 1938.

[14] G. H. Dieke and H. M. Crosswhite, *J. Opt. Soc. Am.*, 33, 425, 1943.

Several automatic controllers have been described that eliminate the major fluctuations in arc current.[15]

A better form of arc for quantitative work and one which is nearly, if not quite, as sensitive is the a-c arc (page 22). It can be used in practically every problem to which the d-c arc is applicable, and, indeed, because of the lower resulting electrode temperature, with some electrode materials that would melt or burn at d-c arc electrode temperatures. For analysis in which high sensitivity is needed, as in trace analysis or the analysis of low concentrations of any kind, it is probably the most useful source. Originally developed by Duffendack and Thompson for the analysis of solutions, it has been adapted to sheet and cast-steel samples by Sawyer and Vincent, to aluminum and magnesium analysis at the Dow Chemical Company laboratories, and to many similar problems. In most applications, the errors can, with care, be kept under 10 per cent and often to about 5 per cent, or less, of the amount determined.

An arc of somewhat similar properties is the Pfeilsticker[16] interrupted arc, which has been widely adopted in industrial applications in Germany: a low-voltage condenser sets up a repeated, arc-like discharge between the electrodes. As in the case of the a-c arc, the electrodes remain cooler than they do in a d-c arc; the repeated striking of the arc tends to initiate discharges from all parts of the electrode tip, and the likelihood of local hot spots and extremes of differential evaporation are thus reduced. These intermittent arc forms are nearly as sensitive as the d-c arc and are useful for quantitative determination of low concentrations.

Where greater accuracy is required without the highest sensitivity, some form of condensed spark source is almost essential. The actual sensitivity attainable by the spark depends on sample composition and form and on equipment, as well as on the spark characteristics, but it is probably always less than the sensitivity attainable by an arc with the same sample and apparatus. The analytical range, however, is greater and, by a choice of two or three line-pairs to cover successive ranges, may often be from a few hundredths of a per cent to 20 per cent, or more. The spark is thus better suited to composition analysis than to trace analysis or inspection.

The simple condensed spark has been used in numerous spectrochemical installations. For certain types of samples, it has proved highly satisfactory. The simple spark, like the arc, however, is subject to erratic fluctuations. These fluctuations seem to be due largely to variation in the number of oscillating arc discharges in the train which follows each spark breakdown (page 25). In some cases, proper choice of the frequency of the spark circuit or the use of a de-ionizing air blast on the spark gap may give sufficient control over the spark.

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[15] E. V. Potter and A. Scott, *Rev. Sci. Instr.*, 18, 722, 1947; G. H. Fetterley and W. M. Hazel, *J. Opt. Soc. Am.*, 40, 76, 1950.

[16] K. Pfeilsticker, *Z. Metallkunde*, 30, 211, 1938.

In many cases of metallic analysis, particularly in the case of steel, adequate control is difficult to attain, and an auxiliary synchronous rotary gap is useful (Fig. 4, page 25). It permits the spark discharge to pass only for a brief interval at the peak of each voltage cycle, while an air blast on the sample gap helps damp the discharge train. Or the rotary gap can be replaced by a fixed gap quenched by a turbulent air blast.

With a source of this type, the installation at the foundry of the Ford Motor Company, described by Vincent and Sawyer,[17] carries out rapid routine analyses of iron and steel, with a probable error in a single determination of the order of 1.5–2.0 per cent. Analysis is made for copper, chromium, manganese, molybdenum, nickel, and silicon, for percentages ranging from 0.1 per cent to 5 per cent, or more. The ranges are set by the demands of the problem; they could be extended by suitable choice of lines and exposure conditions. The errors, of course, arise only in part from source fluctuations; in fact, the source errors here are near their lower attainable limit.

Unless their requirements demand the use of liquid samples or samples that can be excited only in a d-c arc, almost all spectrochemical laboratories now use some form of controlled spark for samples of medium to high concentration, and some form of interrupted or a-c arc for samples of low concentration and for trace or purity determination. Numerous manufacturers supply units that include one or both types. These two sources meet almost all needs and will probably tend to become more standardized in their specifications.

In the use of any of these sources, it is important to study their time-emission characteristics. In arcs, the more volatile elements enter the discharge earlier than the less volatile ones, and the more volatile pass through their peak rate of emission earlier than the less volatile. If the sample is not in pellet form or in a graphite electrode so that it can be completely burned, the interval during which the spectrum is recorded must be carefully chosen. With spark discharges, some preliminary *pre-sparking time*, or *time-of-wait*, is necessary before the spark conditions become stabilized and before radiations from the different constituents of the sample are emitted in a constant and uniform ratio to one another. This time will depend not only on the constituents of the sample, but also on its size and shape, and on the power input to the spark. The larger the cross section of the sample and the smaller the power, the longer the pre-sparking time will be. The pre-sparking time for the controlled spark may vary from a few seconds to as much as a minute, depending on the conditions. The accuracy of the analysis will be greatly affected by the proper choice of these exposure intervals. They must be determined in each case by careful tests.

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[17] H. B. Vincent and R. A. Sawyer, *Metal Progress*, 36, 35, 1939.

13.6. Sample Form and Standard Samples

The accuracy of results may be significantly affected by the size and shape of the electrodes. With the spark, for example, it is desirable to use a size and tip form such that the discharge will play over it in a uniform manner. This effect may be attained by using one flat and one pointed electrode, or two electrodes with blunt, conical tips. The size of the electrodes and the angle of the cone are fixed largely by the power of the spark circuit. Larger electrodes are possible for more powerful outfits. In steel analysis, for a large outfit drawing about 2.5 KVA, electrodes $\frac{7}{32}$ in. in diameter, with conical tips of 148° included angle, have been used. To secure uniformity of electrode size and shape rapidly, most routine industrial laboratories use jigs and grinders. In foundry installations, samples are usually cast from the molten alloy. They should be similar in grain structure to the foundry end-products, and they should set quickly, to avoid differential segregation or loss of the more volatile constituents. It has been found satisfactory to cast them in permanent steel molds, which chill immediately and can be removed at once (Fig. 108). From other solid materials, appropriate electrodes can be cut, sawed, or stamped. Solid electrodes for the arc may be similarly prepared. If the material is in the form of chips or

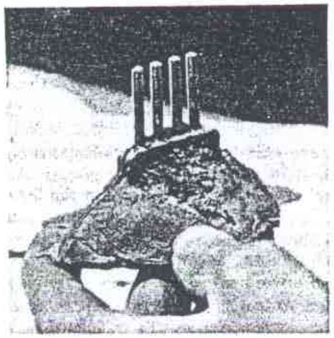

Fig. 108. Chill-cast sample from foundry melt. The sample pins are broken from the sink head for testing.

other irregular pieces, or has inhomogeneities that are significant in relation to the size of the sample to be used, or if it is non-conducting, the sample may be crushed or ground and packed in a hollow graphite electrode. Powdered graphite may be added to improve the conductivity or the burning. Pellets of the powdered material, with or without added graphite, may be formed in hydraulic presses or briquetting machines.

Organic samples can be ashed dry or in acid and placed on graphite electrodes. Liquid solutions can be concentrated, if necessary, and dried on graphite electrodes; they can be sprayed into flames, according to the Lundegårdh method; or they can be sparked in liquid gaps. If there are no lines in a liquid or powdered sample that will give suitable reference lines for the analytical line pairs, some appropriate substance can be added, in solution or otherwise. It is sometimes helpful, too, in arc samples, to add a "buffer," such as an alkali salt, which lowers the arc temperature, reduces the background, and improves the sensitivity.[18]

There is clearly a wide variety of methods for preparing and using samples. The important considerations in selecting sample size and form are:

1. That the sample represents the test material adequately in composition and structure.
2. That the sample will burn satisfactorily in the light source chosen, consuming enough material to average out minor inhomogeneities in sample or test material.
3. That the sample can be calibrated by spectroscopically similar samples of known composition.

Providing standard samples of known composition and spectroscopic similarity is of great importance. Two samples may be considered spectroscopically similar if, for the same composition, they give the same relative line intensities for the lines of all their constituents. For metal samples, the grain size and hardness must usually be the same; for salts or solutions, the acid radical usually must be identical. The presence of a foreign element in one of the samples may make large differences in the relative line intensities. There are many instances of these effects cited in the literature.[19] It is usually most satisfactory to prepare the standard samples in the same manner as the test material, itself, or to make known additions to the test material in order to secure a series of graded standards and then to have careful chemical analyses made. Since the best spectrochemical procedures are now more precise than wet chemical analysis, unless the chemical results are to limit the accuracy, several careful analyses must be made and averaged.

The practical effect of the requirement of spectroscopic similarity is that standard samples of known composition are not very useful and few are available. The National Bureau of Standards has assembled a good assortment of steel samples of varied composition; the Aluminum Company of America has provided some aluminum alloy samples; a few other sets of metal samples have been listed.[20] These samples are valuable for checking procedures and equipment, since their chemical analyses are of high quality, but they can be used to set up analytical curves only if their spectroscopic similarity to the test material has been ascertained.

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[18] For example, R. Mannkopf and C. Peters, *Zeits. f. Physik*, 70, 444, 1931.

[19] Examples and bibliography are given by H. Kaiser, *Zeits. f. angew. Physik*, 1, 1, 1947.

13.7. Selection of Spectrograph

Quantitative spectrochemical analysis can be carried out with any spectrograph of good design that has low scattered and reflected light and affords sufficient dispersion to separate the spectral lines of the samples. It is desirable to attain the separation with a slit width of 20–50 microns, since the resulting line widths lead to smaller microphotometer errors. As large a dispersion as possible is also desirable in line spectrum work, since the continuous or unresolved band-spectrum background is thereby diluted in relation to the line spectrum, and thus background, always troublesome in photometric work, is reduced. On the other hand, spectrographs of smaller dispersion are generally cheaper and faster and may be adequate for spectra which are not too complicated.

Quartz-prism spectrographs are frequently used because many of the elements have their sensitive analysis lines in the ultraviolet regions. For quantitative work, this fact is not often important, because the most sensitive lines are seldom suitable. Quartz instruments, however, have an advantage in industrial laboratories, where there may be dust and corrosive vapors, in that quartz optics resist corrosion and withstand cleaning better than gratings. In the past, a limitation to the use of grating spectrographs has been the lack of an adequate commercial supply. Replica gratings of adequate quality for some types of work are now available, however, and several makers are supplying original gratings of suitable size. The simplicity of grating spectrographs, their large dispersion and resolving power in the visible region, and the current possibility of higher intensity by use of "blazed" gratings has led to their much wider use. Numerous commercial spectrographs are now available.[20A]

13.8. Photographic Emulsion Requirements

Many different types of emulsions have been used. The ideal material should have: high contrast, to give satisfactory sensitivity to concentrational variation; small grain size and low chemical fog, to reduce photometer errors; uniform sensitivity and contrast over a wide spectral range, to avoid the necessity of more than one calibration curve. Such emulsions are usually slow, but low speed is often desirable to permit long enough exposures for good sampling of the material. Contrast and process emulsions satisfactorily fill most of these requirements. The Kodak Spectrum Analysis No. 1 Emulsion, developed especially for the spectrochemistry of metals, combines most of the properties of contrast emulsions with rapid processing, made possible by a thin, hard gelatine layer. This emulsion, however, does not have so long a region of uniform contrast as do some of the other emulsions. It must therefore be used with caution above 3400A or below 2400A. Kodak Spectrum Analysis No. 2 Emulsion has a much longer range (2400A–4400A), of nearly uniform contrast, but a lower contrast than Spectrum Analysis No. 1 Emulsion.

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[20] Standard Samples for Spectrochemical Analysis, *A. S. T. M. Tech. Publ.* No. 58-A, 1947.

[20A] Jarrell, R. F., in *The Encyclopedia of Spectroscopy*, p. 179. Baltimore: Reinhold Publishing Co., 1960. Review of available commercial grating spectrographs. S. S. Berman, P. Tymchuk, and D. S. Russell, *Applied Spectroscopy*, 15, 124, 1961. Discussion of optimum conditions for use of large Ebert spectrograph in spectrochemical analysis.

Whatever the emulsion used, a significant source of experimental error is grain, which leads to variation in microphotometer readings in successive settings on the same line because of the difference in the number of grains included. The uncertainty can be reduced by increasing, as much as possible, the area of the spectral line photometered; the error, in fact, is inversely proportional to the square root of this area. Sawyer and Vincent[21] have shown that by using a photometered area as large as five millimeters long and 50 microns wide, the mean error, under favorable conditions, can be kept as low as 1 per cent.

Errors also arise from variations in emulsion sensitivity from point to point. Since these errors tend to increase with distance, it is highly desirable to have the reference pair of lines close together on the plate—within a millimeter or two if possible.

13.9. Photometric Procedure

Almost any of the methods for the photometric determination of line intensities described in Chap. 12 may be used in quantitative spectrochemical analysis. Since the intensities or relative intensities of comparatively few lines in the spectrum are needed, a spotting, or nonrecording, microphotometer is usually more convenient than a recording instrument.

It is desirable to photometer a considerable length of line, say from three to five millimeters. Such a length can hardly be attained with a rotating-sector method of line weakening. The errors resulting from this method, then, which has been widely used because of its simplicity, will generally not be so small as those from other methods, and, accordingly, it should not be used unless source and other errors make the photometer errors insignificant. Sawyer and Vincent[22] have pointed out that for emulsions that show reciprocity-law failure, the errors introduced by the use of the rotating sector are often by no means negligible, even at high sector speeds. Likewise, intensity marks established by time variation of exposure to a fixed source are under suspicion.

If the calibration marks can be the spectral lines themselves, or marks of similar size, difficulties from the Schwartzschild-Villiger effect in the microphotometer and from the Eberhard effect in the emulsion will be reduced. In most cases of rapid and extensive routine spectrophotometry, time and emulsion will be saved if calibration is made with lines of known relative intensity in the test spectra. From the lines of one of the major matrix elements, lines of invariant relative intensity can be selected that are members of the same multiplet or series or are from the same initial level. The invariance of the line intensity ratios should be checked experimentally, of course. Actually, only one pair of lines of suitable intensity ratio is needed; additional points on the curve can be obtained from one or two more simultaneous spectra made with parts of the slit covered with a neutral filter or a rocking screen of known transmission. For all the plates in one box or in one emulsion lot, the same calibration curve will usually suffice if uniform and mechanical plate-processing techniques are employed. The curve can be checked by reading the ratio of the invariant pair on each individual spectrum and shifting the curve slightly or multiplying the analytical log I ratios by the ratio of the standard to the new invariant log I ratio. It should be noted that since only relative line intensities are required for the analytical curve (Fig. 107), it is not necessary to fix accurately the zero either of intensity or of galvanometer deflection (density). Only differences on these scales are used (see page 274).

As was pointed out in Sec. 13.4, analytical determinations are made by applying the log I ratios of the analysis pair, determined from the emulsion calibration curve, to the previously-determined analytical curve. In large-scale analysis, this reduction is made by means of some form of computing or transposing board that combines a chart of the emulsion curve with a slide-rule scale embodying the analytical curve. Such a board, designed by Sawyer and Vincent, is shown in Fig. 109. The calibration curve is mounted on a drawing board; the log I scale for the curve is on the vertical cursor; on the slider below the curve, the values of the various analytical curves are laid off by projection. Setting the cursor on the microphotometer reading of one line of the analytical pair, adjusting the appropriate analytical scale, and sliding the cursor to the reading of the other line of the pair permits the concentration to be read from the analytical scale. Manufacturers supply various forms of these transposing boards.

Strictly, a particular calibration curve is valid only for a narrow range of wave lengths. In practice, however, the contrast curve of the emulsion is often quite flat over a wide spectral range, and it is found that over this range, the same calibration curve can be used for routine analytical work, without significant error. For example, one curve is often used for Kodak Spectrum Analysis No. 1 Emulsion, from 3400A to 2400A, and sometimes even a little beyond this range.

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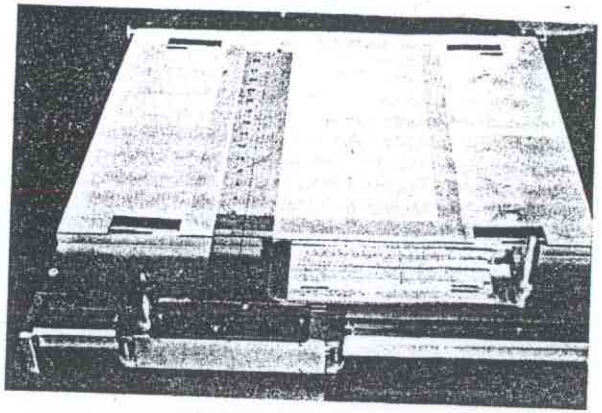
[21] R. A. Sawyer and H. B. Vincent, *J. Opt. Soc. Am.*, 31, 47, 1941.
[22] R. A. Sawyer and H. B. Vincent, *J. Opt. Soc. Am.*, 33, 247, 1943.



posing board, showing calibration curve and analytical scales.

13.10. Magnitude of Errors

The errors which enter into spectrochemical determinations have been discussed in detail by several authors.[23] As in all experimental determinations, the errors are either systematic or random. The systematic errors are caused by such difficulties as faulty analysis of standard samples, plate background, stray light or sensitivity changes in the microphotometer, and incorrect emulsion calibration. Every effort must be made to locate and eliminate, or correct for, these errors. The random errors are all accidental or indeterminate, and are mainly of four kinds: 1, grain effect and variations in photographic emulsion sensitivity; 2, light-source fluctuations; 3, sample inhomogeneities; 4, microphotometer reading errors. The references given describe methods of segregating and evaluating the different random errors. Such evaluation is vital for improving the accuracy of any spectrographic procedure. With care, the microphotometer and emulsion errors can be reduced to 0.2 or 0.3 per cent, each. The controlling errors are usually the sample inhomogeneities and the excitation fluctuations. With proper procedure, except in very unfavorable cases, the mean error of a single observation should not be over 10 per cent. Much work is done regularly with an error of 5 per cent or less. With the best equipment and technique, standard deviations have been reported as low as 1.1 per cent for antimony in lead[24] and 0.8 per cent for chromium in steel.[25] Such results are obtained only for favorable cases, of course, and for concentrations in the range from about 0.5 to 10 per cent. For higher concentrations, the error is likely to be increased by the difficulty of finding analytical lines which are not so dense that they lack sensitivity, while for trace concentrations, there is apt to be difficulty in correcting the weak analytical line for plate background. In most other cases, however, suitable analytical lines can be chosen for the desired range that will give a straight analytical curve of satisfactory slope.

If the analytical lines are properly chosen, the various accidental errors which occur in spectrochemical analysis tend to have a constant percentage relationship to the quantity to be determined, regardless of its size. On the other hand, the errors in gravimetric chemical methods are constant absolute errors. Accordingly, since the absolute spectrochemical errors increase with content, the gravimetric method is relatively better at higher percentages, while the spectrographic method is likely to be better for low and trace analyses. As a rough rule, it may be stated that for the best practice with metallic electrodes, the accuracy of spectrographic analysis is better than that of chemical analysis for concentrations below about 0.5 per cent and approximately the same for those between 0.5 and 10 per cent, but for higher concentrations, chemical wet methods are likely to be more accurate unless special spectrographic techniques are used. Recent industrial applications of spectrochemical methods to the analysis of high alloys of steel and other metals indicate that they give satisfactory precision for the whole range of ordinary industrial practice. In the laboratories of the General Motors Corporation,[26] high-cobalt alloys, up to 29 per cent cobalt, have been analyzed, with a mean deviation of 4 per cent, and Hasler[27] has reported methods for direct analysis of stainless steels and tool steels with an accuracy equal to that of routine chemical methods.

13.11. Speed of Analysis

As to the rapidity of the two procedures, much depends on the type of analysis. Spectrochemical analysis is not so systematized as chemical analysis. That is, it is not possible to specify in advance a general procedure applicable to any or all equipment. Each new kind of sample or element to be determined presents a problem calling for more or less investigation to fix exposure and source conditions, analytical line-pairs, and analytical curve. Once these conditions have been determined, succeeding routine analyses can be carried out expeditiously. Owens[28] has reported results from a large industrial installation showing that the average time required for a determination is only seven man-minutes, while the chemical methods previously employed took at least four times as long. Vincent and Sawyer[29] have described a large installation for iron and steel analysis that makes it possible for a high-precision analysis of a sample for as many as six minor constituents to be completed and reported in six minutes, and for two shifts of four operators each to handle over 300 samples in a 16-hour day.

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[23] H. Kaiser, *Zeits. f. tech. Physik*, 17, 227, 1936; R. A. Sawyer and H. B. Vincent, *J. Opt. Soc. Am.*, 31, 47, 1941; 32, 686, 1942; H. H. Grossman, R. A. Sawyer, and H. B. Vincent, *J. Opt. Soc. Am.*, 33, 185, 1943; H. Kaiser, *Spectrochim. Acta*, 3, 278, 1948.

[24] H. Kaiser, *Zeits. f. tech. Physik*, 17, 227, 1936.

[25] H. B. Vincent and R. A. Sawyer, *J. Opt. Soc. Am.*, 32, 686, 1942.

[26] Y. I. Sihvonen, D. L. Fry, R. E. Nusbaum, and R. R. Baumgartner *J. Opt. Soc. Am.*, 39, 257, 1949.

[27] M. F. Hasler, *J. Opt. Soc. Am.*, 39, 1062A, 1949.

13.12. Direct-Reading Spectrochemical Methods

Although modern techniques have greatly speeded up routine spectrochemical procedures and simplified them so that they can be carried out by technicians without specialized education, there is an increasing field in large-scale control laboratories for automatic, direct-reading installations. Various investigators have worked on the development of such equipment, using as the detecting element either a Geiger counter or a photomultiplier tube.

One of the earliest applications of the Geiger counter was by Duffendack and Morris,[30] who studied its possibilities for the detection of spectral lines. Continuation of their work by Hanau and Wolfe[31] led to an installation at the Ford Motor Company that has been described by Nahstoll and Bryan.[32] It uses the 2136A line of phosphorus, which is below the optimum wave-length range for the photographic method, for the routine determination of phosphorus in cast steel.

Thanheiser and Heyes[33] made an early application of the photocell, using a spark discharge in the analysis of aluminum alloys. The first large installation using photocells was built at the Dow Chemical Company for the analysis of magnesium alloys, by Saunderson and his associates.[34] It incorporates a spark source and a grating spectrograph. At the focus of the various analysis lines, small prisms reflect the light to photomultiplier tubes. The photocurrents charge individual condensers,

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[28] J. S. Owens, *Ind. & Eng. Chem.*, **10**, 64, 1938.
[29] H. B. Vincent and R. A. Sawyer, *Metal Progress*, **36**, 35, 1939.
[30] O. S. Duffendack and W. E. Morris, *J. Opt. Soc. Am.*, **32**, 8, 1942.
[31] R. Hanau and R. A. Wolfe, *J. Opt. Soc. Am.*, **37**, 989, 1947.
[32] G. A. Nahstoll and F. R. Bryan, *J. Opt. Soc. Am.*, **38**, 510, 1948.
[33] N. G. Thanheiser and J. Heyes, *Spectrochim. Acta*, **1**, 270, 1939.
[34] J. B. Saunderson, V. J. Caldecourt, and E. W. Peterson, *J. Opt. Soc. Am.*, **35**, 681, 1945.

which, at the end of the sparking time, are discharged through resistances that actuate d-c amplifiers, and the quantity stored is recorded in terms of the amount of each constituent, on separate dial recorders. Corrections are automatically made for spectrum background and for photocell dark current. The phototube assembly has up to sixteen exit slits and photomultiplier tubes. Since one tube is required for the internal standard and one for an automatic servo monitor to maintain optical alignment, up to fourteen unknown elements can be recorded simultaneously. The complete analysis is recorded in 40 seconds with a mean deviation of from 1 to 2 per cent. The equipment is produced by Baird-Atomic, Inc.[35]

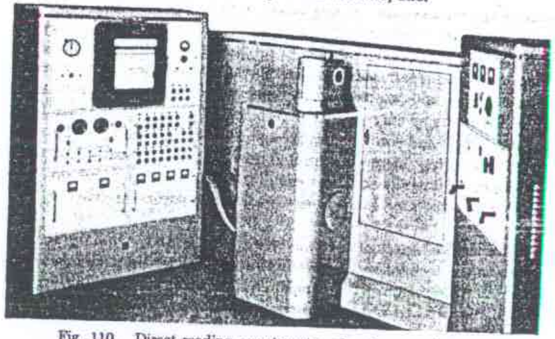

Fig. 110. Direct-reading quantometer, showing recorder console (left), arc-spark stand (center), and source unit (right). (Courtesy of the Applied Research Laboratories.)

Somewhat similar equipment has been developed by the Applied Research Laboratories for use with their 1.5-meter and 2-meter grating spectrographs.[36] Small mirrors reflect the light to the photomultiplier tubes, and as many as 16 such receivers can be mounted on the focal curve of the spectrograph. The accumulated condenser charges from the phototubes are amplified and then recorded by a pen recorder. The equipment is called a Quantometer and is supplied either in the form of an adapter, to be applied to an existing spectrograph-and-light-source installation, or as a completely self-contained system, with source, grating, and receiving and recording equipment. The control features of the complete outfit are shown in Fig. 110.

These large automatic installations are much more expensive than photographic equipment. They can, however, deliver a complete analysis of a sample in one minute or less, at a large saving in operator's time per analysis. Their extra cost and complexity are justified in laboratories where hundreds of analyses are made daily, and especially where melting or furnace operations are controlled by spectrographic analysis, and expensive furnace time can be saved by their speed.

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[35] R. O'B. Carpenter, E. DuBois, and J. Sterner, *J. Opt. Soc. Am.*, **37**, 707, 1947.
[36] M. F. Hasler and H. W. Dietert, *J. Opt. Soc. Am.*, **34**, 751, 1944. M. F. Hasler, R. W. Lindhurst, and J. W. Kemp, *J. Opt. Soc. Am.*, **38**, 789, 1948.

These outfits require electronic circuits of great stability and need highly accurate temperature control to prevent wandering of the line maxima from the narrow receiving mirrors or prisms as a result of thermal effects on the dispersion. Furthermore, the size of the receiving elements limits the number of the possible receivers, and the closeness of spacing. It would appear that they could be simplified by using only one receiver and traversing the spectral lines past the receiver, in turn, by rotating the dispersing element, as is done in infrared spectrophotometers. This procedure would read the different elements successively, instead of simultaneously, and would require a light source of uniform characteristics. In practice, only the hollow-cathode, some high-frequency vapor discharge lamps, and some flames are sufficiently stable sources for scanning instruments. They have very limited application. Almost all commercial spectrochemical installations use simultaneous observations of the lines of interest and integrate the intensity over an exposure of from 10 to 100 seconds.

The sensitive lines of carbon, phosphorus, and sulphur, important elements in the technology of ferrous alloys, occur in the region from 2000A to 1600A. This region is a difficult one for photographic photometry but is easily accessible to photomultiplier techniques. Several makers supply direct-reading equipment for this region. The evacuated spectrograph is usually separated from the sample stand by a thin fluorite window, and the light source is a controlled arc in argon which is used to flush out the oxygen of the atmosphere when the sample is changed.

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